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Application Oriented New Materials by Spray Forming

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Abstract

The development of new materials and processes is projected to be the prime mover for the 21st century. Rapid solidification process was developed in 1960s and gained tremendous interest from the research community. Similarly, spray forming, one of the variants of rapid solidification, was observed as a promise for the synthesis of bulk materials that could not be generally processed by conventional route. As spray forming has already been a well established process and has witnessed commercial production, the present paper attempts to investigate the possibility of employing this technique to produce bulk amorphous / nanocrystalline / quasicrystalline materials, which have shown unprecedented physical and mechanical properties. The effect of process parameters and mechanisms involved in the formation of these materials in bulk has been brought out.

Introduction

The global concern on the economic growth of manufacturing sector and the role of processes, leading to value addition, on environmental degradation have prompted the development of novel, efficient, low-energy-intensive and economically viable processes. On the other hand, the stringent requirements on the physical, mechanical and chemical properties of materials have culminated into an ever increasing effort by researchers to design new materials and non-conventional processes. One of the major breakthroughs in this direction was the development of rapid solidification process by Duwez et al. [1] in 1960, where a cooling rate of the order of 10^7 K/s could be achieved for liquid to solid transformation that resulted in bypassing the nucleation and growth of crystalline phases. The amorphous liquid-like structure thus obtained showed unprecedented and unique properties [2-5]. The advent of rapid solidification led to the development of several new amorphous, nano-crystalline and quasicrystalline metallic materials that revealed properties which could not be realized through the conventional processes. In addition, new material compositions were found that did not require rapid solidification for amorphization e.g. Pd-, Zr-, Ti-based glass forming materials. However, some of the systems such as Al-, Mg-, Fe-, Cu-based materials do require comparatively high cooling rate for amorphization directly from the liquid state. Although the rapid solidification technique has been extensively employed for academic curiosity on the structure and properties of the ensuing materials, it suffers from limitations so far as the application is concerned. The major drawback lies in the fact that such a high cooling rate (10^3-10^6 K/s) for compositions with low glass forming ability limits at least one of the dimensions of the solidifying material, which can vary from a few hundred microns to a few millimeters only, so that a high surface area to volume ratio is achieved.

Spray atomization and deposition is one of the processes developed in 1970s that led to the development of novel materials in bulk, which were not possible to be processed by conventional routes. The inherent rapid solidification effect during melt atomization stage and the unique mechanism of microstructural evolution during deposition of semi-solid/liquid droplets on a substrate lead to refined and homogeneous microstructure engendering unprecedented properties [6-7]. In the following sections, therefore, the possibility of the formation of bulk amorphous/partially amorphous, nanocrystalline and quasicrystalline materials by spray forming has been investigated in light of recent studies.

Spray forming (SF) process

Spray forming is a well established process [6-10] which has already witnessed commercial scale production for the last 15-20 years. Spray forming consists of two distinct but integral processes of gas atomization of a melt and deposition of the ensuing spray of droplets onto a substrate. A wide size range of droplets are produced during atomization stage that experience high cooling rate, depending upon the size of droplets. However, the degree of undercooling of the droplets is governed not only by the cooling rate but also the presence of potential catalytic nucleants. During disintegration of the melt stream the total number of potential nucleation sites is divided into various droplets leaving large fraction of droplets free of nucleants, particularly when the mean droplet size is small, thereby increasing the possibility of high undercooling in the nucleant free droplets [11-12]. The deposition of undercooled/ partially solidified droplets on a substrate leads to fragmentation of droplets creating a large number of dendrite debris that act as nucleation sites for further solidification. This gives rise to refined and equiaxed grain morphology. The microstructure of the deposit can be tailored by selecting appropriate process parameters. The parameters such as melt flow rate, gas flow rate, nozzle design, gas pressure, deposition distance, substrate material, substrate temperature, substrate surface condition have a complex interplay in determining the deposit microstructures. Depending upon the surface temperature of a growing deposit the incoming undercooled droplets may experience a high cooling rate akin to splat cooling. Lower the surface temperature higher will be the cooling rate as the droplets splat on the growing deposit.

Amorphous/Nano-crystalline materials by spray forming

The amorphisation and/or nanocrystallisation of liquid alloys depend to a large extent on the cooling rate that suppresses the crystallization phenomenon. However, the alloy composition determines the critical cooling rate for amorphisation or the glass forming ability (GFA). The formation of bulk amorphous materials is easier for the compositions with high GFA, however, those with low GFA such as Al-, Mg-, Fe- and Cu-based alloys show high critical cooling rate for amorphisation. Although gas atomization technique has successfully been employed for producing amorphous powders of alloys with low GFA, the consolidation of these powders to achieve bulk glassy/nanocrystalline materials, from application point of view, is still a challenge.

In view of the above, spray forming has been sought as one of the processes to synthesise bulk amorphous or nanocrystalline materials. The first report on the development of amorphous materials by spray deposition was published by Oguchi et al. in the year 1990 [13-14] on $Al_{84}Ni_{10}Mm_6$ system. In this experiment, a high pressure gas atomization process was used to atomise the melt at 9.8 MPa pressure and the deposition was done on a rotating copper substrate, with diameter 250 mm, with minimum speed of 4000 rpm. A fully amorphous sheet of 7 mm was produced with characteristics similar to melt spun ribbons of the same composition. This was attributed to a two stage liquid quenching technique. The process utilizes the delayed crystallization of undercooled droplets of glass forming melts and their subsequent layer by layer deposition on the growing deposit to give rise to bulk amorphous/partially amorphous materials, where the undercooled droplets splat on the deposit surface experiencing a high solidification rate. Figure 1 shows the optical micrographs of the crystalline, partially crystalline and amorphous overspray powders of $Al_{85}Y_8Ni_5Co_2$ generated during the process. The overspray powders consist of a large fraction of amorphous powders, particularly in the smaller size range (fig. 1a). The powders in the size range of 25-50 μm revealed that the crystallization commences, primary phase formed and the remaining liquid solidified amorphous/nanocrystalline (as shown by arrow in fig. 1b). Large size particles, above 100 μm size, mostly showed fully crystalline particles.

The DSC analysis of the powders [15] as well as the deposits, as shown in fig. 2, revealed that the crystallization energy, from the first DSC peak, associated with the powders in the size range of 50-75 μm is lower than that observed even in the top of the deposit. The deposit thickness in this case was 12 mm. This indicated that the amorphisation is more effective in the deposit compared to the atomization stage. It is worth considering that only overspray powders have been compared with the deposit, whereas, a major fraction of droplets that hit the substrate to form the deposit is in the size range of 200-600 μm. It can, therefore, be argued that the amorphisation in the deposit takes place by a second cooling stage that is high enough to lead to amorphisation.

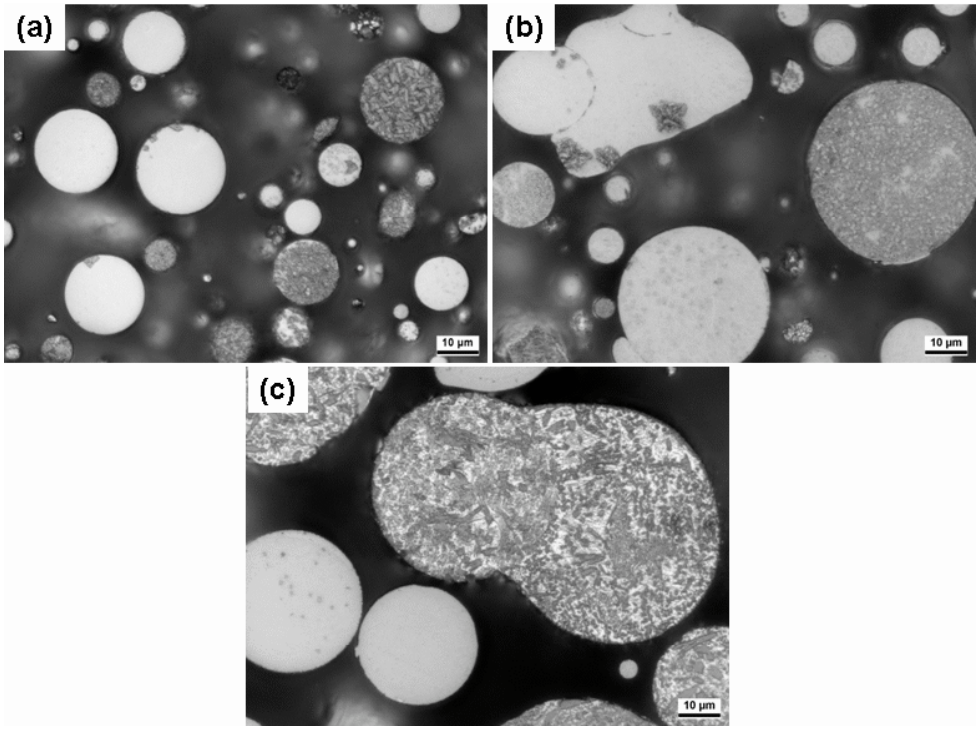

Figure 1. Optical micrographs of overspray powders of $Al_{85}Y_8Ni_5Co_2$ in the size range (a) -25 µm (b) -50+25 µm and (c) -75+50 µm.

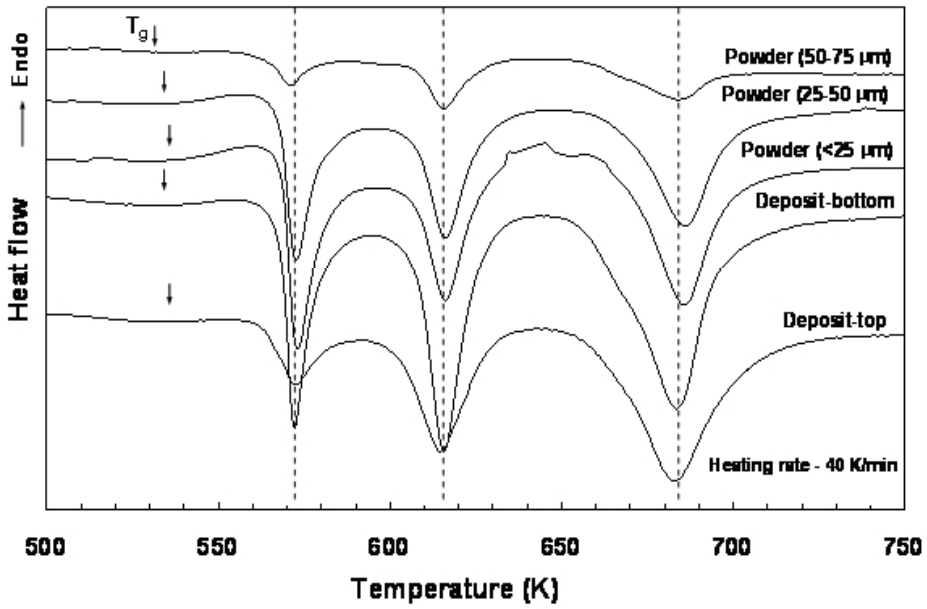

Figure 2. DSC plots of overspray powders and the deposits revealing a marked difference in the first crystallization energy of deposit and the powder in the size range 50-75 µm [15].

Subsequent to the first demonstration by Oguchi et al. [13-14], partial amorphisation of Al-based system by spray forming was reported by Afonso et al. [16] in the year 2001. This followed by several studies on amorphisation of Al-, Fe- and Mg-based systems. A list of recent works on Al-based system is given in Table 1. In all these studies, most of the investigators were successful in demonstrating the presence of high fraction of amorphous phase in the deposit. However, there was found to be a large discrepancy in the results, as the process of amorphisation by conventional spray forming was not clearly understood due to the fact that a large number of variables are involved in the process. The most significant part of these investigations were the understanding that a cold substrate or a high gas to metal ratio, which in turn gives rise to a fine droplets in the spray, would give rise to amorphisation. However, Srivastava et al. [15] attempted to employ a pre-heated substrate so as to make use of the thermal conduction through the substrate to achieve rapid heat extraction from the deposit. And also, in this investigation, the deposit was 10-12 mm plate instead of billet. It is a prerequisite for amorphisation to take place that glass forming undercooled droplets should form a splat after deposition and the deposit surface temperature should be low enough to engender high cooling rate [18]. Fig. 3 shows the optical micrographs of slow cooled material and spray formed deposit. It is clearly visible that the microstructure of the material with low cooling rate consists of coarse primary intermetallic phases along with eutectic constituents. In contrast, the deposit reveals a large fraction of featureless regions. These featureless regions are the amorphous/nanocrystalline areas, which are not resolvable at optical resolution.

Table 1: A list of recent investigations on spray forming of Al-based systems

Alloy	Thickness/ amount sprayed	Amorphous fraction (%)	Characteristic phases	Year [Ref.]
$Al_{84}Ni_{10}Mm_6$	7 mm	Sheet – 100%	Amorphous	1990-1991 [13,14]
$Al_{84}Y_3Ni_8Co_4Zr_1$	2.1 kg	Billet- Crystallised Overspray-40%	fcc-Al, Al_3Zr, Al_9Co_2, $Al_{16}Ni_3Y$	2001[17]
$Al_{85}Y_8Ni_5Co_2$	7.0 kg	Billet - 76% (G/M ratio :10 m^3/kg)	a-Al, Al3Y, Al2Y, Al_9Co_2, $Al_{16}Ni_3Y$	2001[16]
$Al_{89}La_6Ni_5$	3 mm	Sheet - 36%	fcc-Al, Al_3Ni, $Al_{11}La_3$ and some unknown phases.	2005[20]
$Al_{85}Nd_5Ni_{10}$	30 mm	Billet – crystalline Overspray – 63%	a-Al, Al_6NdNi_2, Al_3Ni, Al_6NdNi_2 (secondary Crystals),	2006[21]
$Al_{89}La_6Ni_5$	1-2 mm	Sheet – 36%	fcc-Al, Al_3Ni, $Al_{11}La_3$	2007 [22]
$Al_{85}Y_8Ni_5Co_2$	12 mm	Bottom – 83%, Top – 56%	fcc-Al, Al_2Y and Al_3Y, $Al_{23}Ni_6Y_4$	2009-2010 [15,19]
$Al_{83}La_5Y_5Ni_5Co_2$	8 mm	Partially amorphous	a-Al, Al3Y, Al11La3, Al3Ni and unknown phases	2009 [23]
$Al_{86}Si_{0.5}Ni_{4.06}Co_{2.94}Y_6La_{0.5}$	12 mm	Bottom – 91.7%, Middle – 78% Top – 54.3%	fcc-Al and Al_4NiY	2011[24]

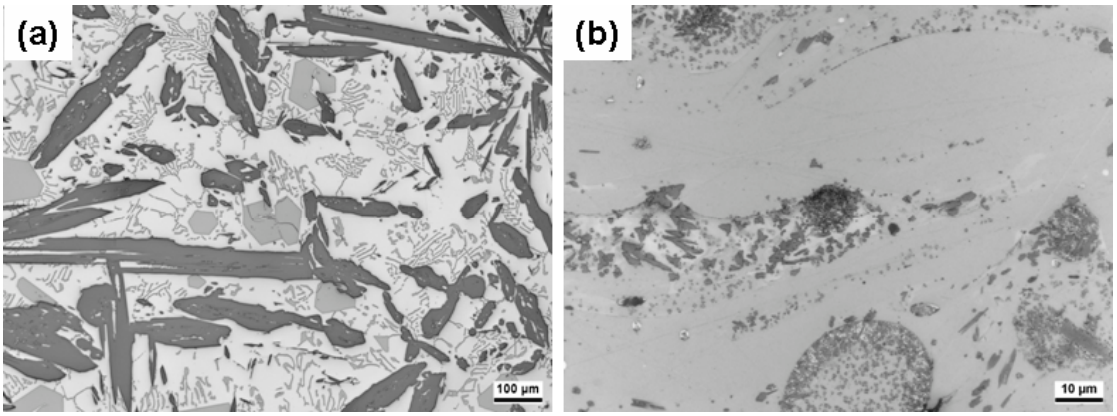

Figure 3. Optical microsgraphs showing (a) a coarse microstructure of slow cooled and (b) a large fraction of featureless region in spray formed deposit of $Al_{85}Y_8Ni_5Co_2$.

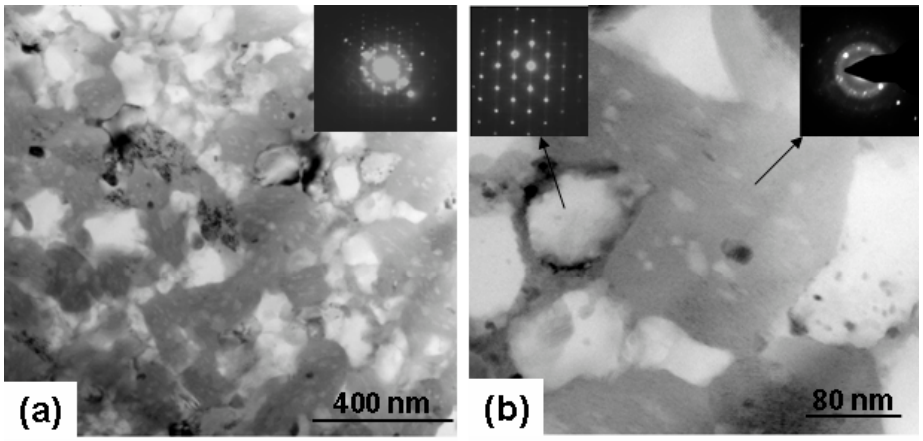

Figure 4. TEM micrographs showing (a) large (100-200 nm) α-Al grains in an amorphous matrix and (b) a magnified view revealing amorphous phase in grey and 10-20 nm size α-Al precipitates [15].

A further investigation on the spray formed alloy by X-ray diffraction analysis, SEM and TEM revealed [15, 19] that the deposit consisted of primary intermetallic phases, nanocrystalline regions nearby the intermetallic interface and highly refined nanocrystalline or amorphous phase. The basic mechanism causes such microstructural characteristics of the deposit is the deposition of undercooled droplets on a cold surface and thereby making a splat in the thickness range of 40-50 µm. The high cooling rate of the splats leads to amosphisation of the undercooled liquid. However, as the spray consists of a wide size range of droplets, a large fraction of these droplets witness commencement of crystallisation prior to deposition on the substrate. Due to high viscosity of glass forming liquids the heat of crystallization is not efficiently transferred to the bulk of the droplets and a considerable amount of liquid remains in the undercooled state prior to deposition. This engenders the presence of a large fraction of amorphous or nanocrystalline phase in the deposit. It has been observed that the average amorphous fraction in the deposit varies in the range of 60-70% [15]. Fig. 4 shows the TEM micrographs of spray deposited $Al_{85}Y_8Ni_5Co_2$ revealing amorphous phase in grey contrast and α-Al phase in white. The amorphous phase also contains 10-20 nm size α-Al particles which have been identified as precipitates from the crystallization of amorphous phase.

A schematic of the droplet conditions in the spray and the mechanism of droplet deposition on the substrate/growing deposit are given in figure 5, which is self explanatory.

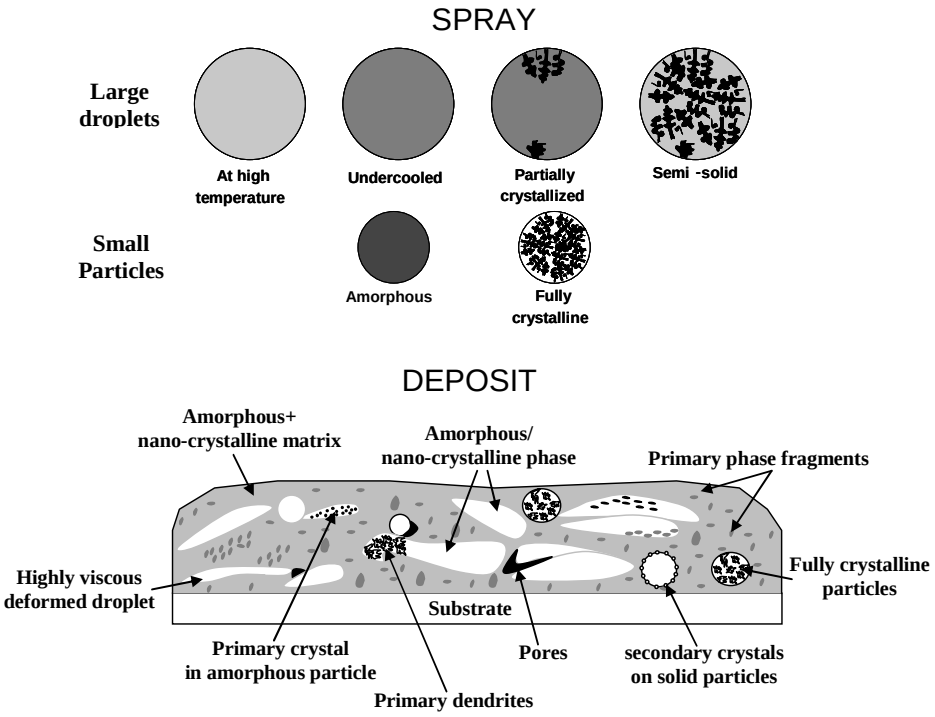

Figure 5. A schematic of the mechanism of deposition and droplet conditions during spray forming of glass forming alloys.

It can be concluded from the above results that the synthesis of bulk nanocrystalline/amorphous materials can be possible by spray forming. However, the selection of process parameters should favour a narrow size distribution of droplets in the spray, a high cooling rate and low heat content in the spray prior to deposition. The substrate should be capable of extracting high heat content of the deposit to avoid temperature build up and thereby crystallization of amorphous phase and the deposition surface should be cold for high cooling rate of splats but hot enough to avoid high porosity generation in the deposit.

Quasicrystalline materials by spray forming

Quasicrystalline materials are characterized as aperiodic long-range ordered solids, which gives rise to several distinctive properties such as high hardness, low thermal conductivity, high corrosion and oxidation resistance and low coefficient of friction [25]. It has been observed that Al-Cu-Fe alloy, with the composition in the range of 58-70 at.% Al, 20-28 at.% Cu and 10-14 at.% Fe, forms stable quasicrystals during conventional casting by a peritectic reaction. Several attempts have been made to synthesise quasicrystals since its first discovery in 1984. In general, the processing routes for such materials are restricted to melt spinning [26], melt atomization [27-28], mechanical alloying [29-33] and plasma spraying [34]. Although conventional casting route shows the formation of stable quasicrystals (QC) in Al-Cu-Fe system, a single phase bulk quasicrystalline materials has still eluded the investigators.

The inherent rapid solidification effect in spray forming process, as described in section 2, has been observed to alter the sequence of solidification based on the degree of undercooling of droplets. In addition, the layer by layer deposition of undercooled droplets gives rise to bulk deposit. Therefore, an attempt was made to synthesise bulk quasicrystals of $Al_{62.5}Cu_{25}Fe_{12.5}$ (at%) by spray forming.

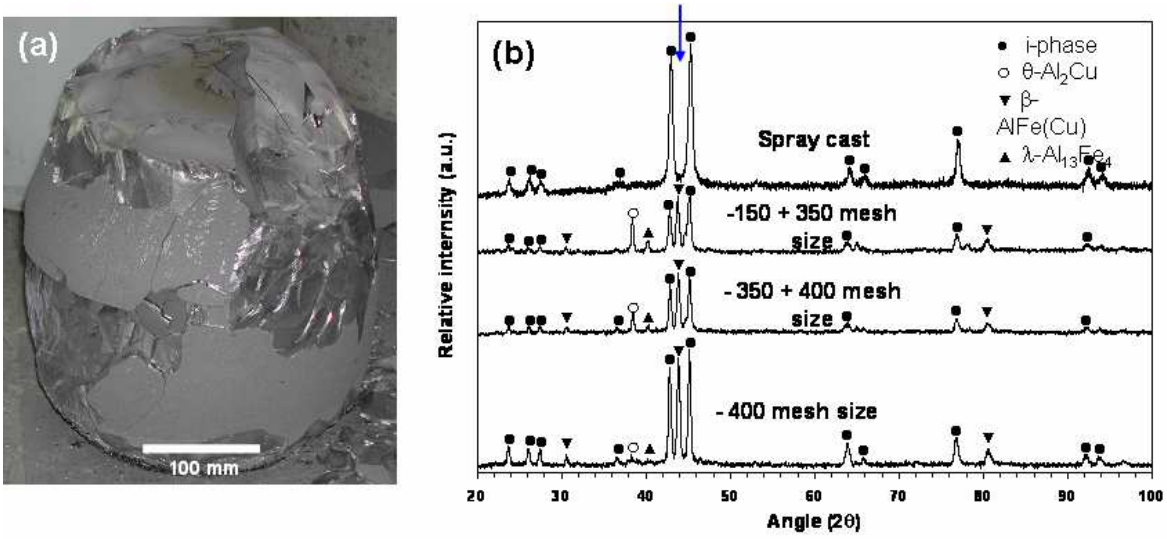

Figure 6. (a) The spray single phase quasicrtalline (QC) billet (b) x-fdiffractogram showing single phase QC compared with overspray powders [35].

Figure 6a shows the single phase quasicrystal deposit billet of the size of 200 mm diameter and approximately 400 mm height (~40 kg). Fig. 5b shows the x-ray diffraction pattern of the billet and the overspray powder particles of different sizes. It is obvious from the figure 6b that the deposit consists of a single phase icosahedral quasicrystal. However, the overspray powder particles of the smallest size (-400 mesh), which would experience a high cooling rate during atomization due to large surface to volume ratio, reveal a strong peak from the β-phase. This is indicative of the fact the not only the high cooling rate is responsible for the formation of single phase quasicrystals but also the unique mechanism of microstructural evolution in spray forming plays a crucial role.

Pseudo binary Al-Cu-Fe phase diagram and TTT curves [25] indicates that a high cooling rate and pronounced undercooling of droplets may lead to suppression of peritectic reaction and to the formation of icosahedral quasicrystalline materials directly from the undercooled melts. However, as the spray contains a wide size range of droplets, a considerable fraction of droplets may lead to formation of primary phase λ-$Al_{13}Fe_4$ and β-AlFe(Cu), particularly large droplets with high heat content. The fragmentation of these phases upon deposition results in a uniform distribution of these small particles in the liquid pool. As the temperature of the liquid pool remains moderate, as a large amount of heat is already extracted in the spray, stable quasicrystalline phase is formed during deposition. The high temperature of the billet post-deposition is expected to lead to transformation of remnant fraction of small size λ-$Al_{13}Fe_4$ and β-AlFe(Cu) phases into quasicrystalline phase.

Figure 7a shows the optical micrographs of the deposit revealing the layered structure consisting of two different microstructural features (a) fine grains and (b) coarse grains with λ-phase and shrinkage pores. Figures 7b and 7c are the higher magnification micrographs of fine and coarse grain regions suggesting that the fine grain areas do not contain second phase. However, the regions with large grains consist of λ-phase within the grains and shrinkage porosity at the grain boundaries. After heat treatment of the samples for a small duration, compared to long time heat treatment for as cast materials, all the λ-phase transform to icosahedral quasicrystal. A large number of annealing twins were observed, particularly in the coarse grain regions. The hardness of the deposit was found to be 10.6 GPa and 9.33 GPa at the loads of 50 and 100 gm, respectively.

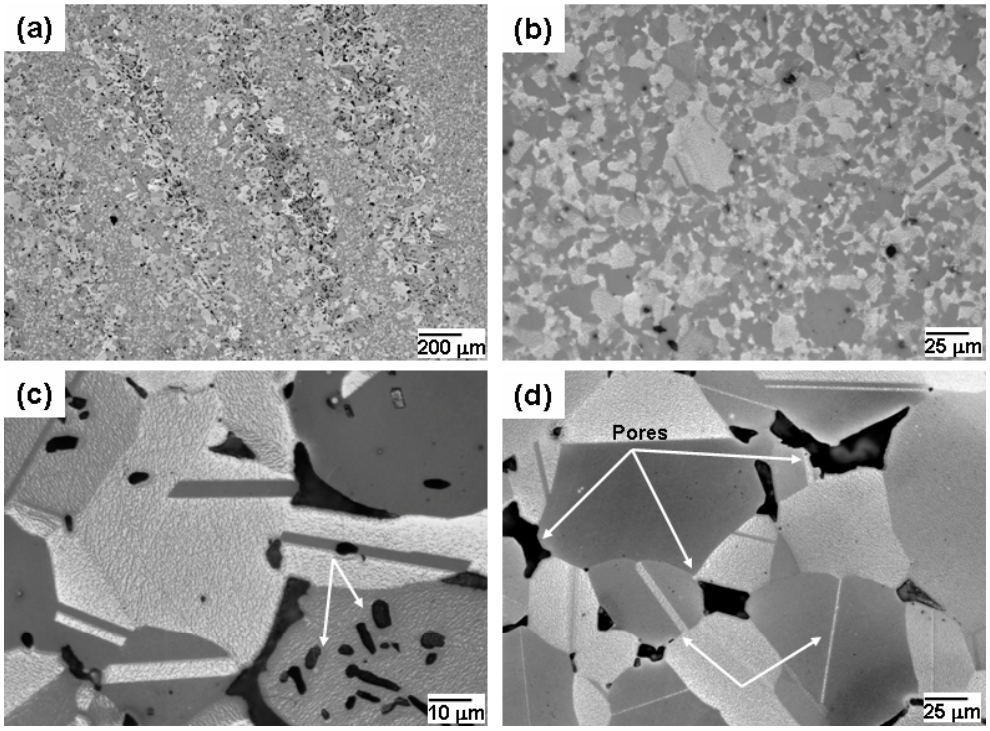

Figure 7. Optical micrographs of deposit showing (a) layered structure of fine and coarse grains with some λ-phase in black contrast (b) fine grains (c) λ-phase within grains and (d) absence of λ-phase after heat treatment.

Conclusions

The above detailed discussion reveals that spray atomization and deposition is a potential materials processing technique that can be successfully utilized to produce bulk nano-crystalline/amorphous/ quasicrystalline materials. The inherent rapid solidification effect during the atomization stage and the unique microstructural evolution mechanism during deposition play a determining role in designing new materials, which were not possible by conventional routes.

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